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14. ABSTRACT
Extensive research has been conducted in growing and characterizing semiconductor nanowires, especially in demonstrating unique lasing capabilities of our nanowire materials and structures. The key results achieved include a novel growth method strategy that is termed "dual-gradient method". This dual gradient method has been utilized to grow a wide range of novel alloy semiconductor nanowires and led to a wide array of new nanomaterials such as first quaternary semiconductor alloy nanowires, spatial-composition graded alloy nanowires with emission covering

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Topic 4.2 Optoelectronics: Continuously
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ABSTRACT

Extensive research has been conducted in growing and characterizing semiconductor nanowires, especially in demonstrating unique lasing capabilities of our nanowire materials and structures. The key results achieved include a novel growth method strategy that is termed "dual-gradient method". This dual gradient method has been utilized to grow a wide range of novel alloy semiconductor nanowires and led to a wide array of new nanomaterials such as first quaternary semiconductor alloy nanowires, spatial-composition graded alloy nanowires with emission covering the complete visible spectrum emission from a single substrate, and widely tunable lasing on a single substrate from 500 to 700 nm. More recently the further exploration of such growth has led to the first dual-color (red and green) lasing from a single nanosheet and dynamically tunable color lasing between green and red from a single nanowire. The second part of the work for the extension period involved investigation of electrical injection single nanowire laser work. Extensive design and fabrication study has been conducted. While our designs have shown great promise and various fabrication steps have been verified, a working electrical injection laser has not been achieved. We believe that we have gained a lot of understanding of the issues involved.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
11/14/2009	1.00	Anlian Pan, Weichang Zhou, Eunice S. P. Leong, Ruibin Liu, Alan H. Chin, Bingsuo Zou, C. Z. Ning. Continuous Alloy-Composition Spatial Grading and Superbroad Wavelength-Tunable Nanowire Lasers on a Single Chip, Nano Letters, (01 2009): . doi:
TOTAL:		**1**

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper
TOTAL:	

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. P. L. Nichols, Z. Liu, L. Yin, and C. Z. Ning, CdxPb1-xS Alloy Nanowires and Heterostructures with Simultaneous Emission in Mid-Infrared and Visible Wavelengths

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Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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Received   Paper

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Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received		Paper
09/08/2011	6.00	Cun-Zheng Ning, Derek Caselli. High-performance laterally-arranged multiple-bandgap solar cells using spatially composition-graded CdxPb1-xS nanowires on a single substrate: a design study, Optics Express (07 2011)
09/08/2011	7.00	Hua Wang, Minghua Sun, Kang Ding, Martin T. Hill, Cun-Zheng Ning. A Top-down Approach to Fabrication of High Quality VerticalHeterostructure Nanowire Arrays, Nano Letters (03 2011)
09/08/2011	5.00	Anlian Pan , Patricia Nichols, Cun-Zheng Ning. Semiconductor alloy nanowires and nanobelts with tunable optical properties , IEEE JOURNAL OF SELECTED TOPICS IN QUANTUM ELECTRONICS (09 2011)
11/14/2009	3.00	A.L. Pan, R.B. Liu, M.H. Sun, C.Z. Ning. Spatial Composition Grading of Quaternary ZnCdSSe Alloy Nanowires with Tunable Light Emission Between 350 nm and 710 nm on a Single Substrate, (11 2009)
11/14/2009	4.00	C.Z. Ning, A.L. Pan, and R.B. Liu. SPATIALLY COMPOSITION-GRADED ALLOY SEMICONDUCTOR NANOWIRES AND WAVELENGTH SPECIFIC LATERAL-MULTIJUNCTION FULL-SPECTRUM SOLAR CELLS, (06 2009)

TOTAL: **5**

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Books

Received Paper

TOTAL:

Patents Submitted

Laterally Varying II-VI Alloys and Uses Thereof

Patents Awarded

Awards

C.Z. Ning, IEEE Photonic Society Distinguished Lecturer (2009)
C.Z. Ning, OSA Fellow, 2013
C.Z. Ning, IEEE Fellow, 2013

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
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Minghua Sun	0.50	
FTE Equivalent:	**1.00**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Cun-Zheng Ning	0.05	
FTE Equivalent:	**0.05**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 1.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 1.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 1.00

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Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME
Patricia Nichols
Minghua Sun

Total Number: **2**

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment

Technology Transfer

Annual Report on Project entitled

Continuously spatial-wavelength-tunable nanowire lasers on a single chip

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Report period: August 1, 2008 - July 31, 2013

Papers in Peer-Reviewed Journals:

1. A. Pan, W. Zhou, E. Leong, A. Chin, R. Liu, B. Zou, C. Z. Ning, Continuous Alloy-Composition Spatial Grading and Superbroad Wavelength-Tunable Nanowire Lasers on a Single Chip, Nano Letters, 9, 784 (2009)
2. A. L. Pan, R.B. Liu, M.H. Sun, and C.Z. Ning, Quaternary Alloy Semiconductor Nanobelts with Bandgap Spanning the Entire Visible Spectrum, J. Am. Chem. Soc. (Communication), 131, 9502 (2009)
3. M.H. Sun, E.S.P. Leong, A.H. Chin, C.Z. Ning, G.E. Cirlin, Yu.B. Samsonenko, V.G. Dubrovskii, L. Chuang, and C. Chang-Hasnain, Photoluminescence properties of InAs nanowires grown on GaAs and Si substrates, Nanotechnology 21, 335705(2010)
4. A. L. Pan, R.B. Liu, M.H. Sun and C.Z. Ning, Spatial composition grading of quaternary alloy ZnCdSSe nanowires with tunable light emission between 350 nm and 710 nm on a single substrate, ACS Nano, 4, 671-680(2010)
5. C.Z. Ning, Semiconductor Nanolasers, (Invited Tutorial), Phys. Stat. Sol B247, 774-788 (2010)
6. D. A. Caselli and C.Z. Ning, High-performance laterally-arranged multiple-bandgap solar cells using spatially composition-graded $Cd_xPb_{1-x}S$ nanowires on a single substrate: a design study, Optics Express, Vol. 19, S4, pp. A686-A694(2011)
7. H. Wang, M.H. Sun, K. Ding, M. T. Hill, and C.Z. Ning, A Top-down Approach to Fabrication of High Quality Vertical Heterostructure Nanowire Arrays, Nano Lett., 11, 1646-50 (2011)
8. Jae Cheol Shin, Kyou Hyun Kim, Ki Jun Yu, Hefei Hu, Leijun Yin, Cun-Zheng Ning, John A. Rogers, Jian-Min Zuo, and Xiuling Li, InxGa1⁻xAs Nanowires on Silicon: One-Dimensional Heterogeneous Epitaxy, Bandgap Engineering, and Photovoltaics, Nano Lett., 11, 4831, 2011.
9. A. Pan, L. Yin, Z.C. Liu, M.H. Sun, R.B. Liu, P. L. Nichols, Y. Wang, and C. Z. Ning, "Single-crystal erbium chloride silicate nanowires as a Si-compatible light emission

material in communication wavelengths", *Optical Material Express*, Vol. 1, No. 7, pp. 1202-1209, 2011.

10. P. L. Nichols, M.H. Sun and C.Z. Ning, Influence of Supersaturation and Spontaneous Catalyst Formation on the Growth of PbS Wires: Toward a Unified Understanding of Growth Modes, *ACS. Nano*, 5 8730 （2011）.
11. A. Pan, P.L. Nichols, and C.Z. Ning, Semiconductor alloy nanowires and nanobelts with tunable optical properties (invited), IEEE-JSTQE on Nanowires, 17, 808 (2011)
12. L. Yin, H. Ning, S. Turkdogan, Z. Liu, P. L. Nichols, and C. Z. Ning, Long lifetime, high density single-crystal erbium compound nanowires as a high optical gain material, Appl. Phys. Lett., 100, 241905(2012)
13. M.H. Sun, H. J. Joyce, Q. Huang, H.H. Tan, C. Jagadish, C. Z. Ning, Removal of Surface States and Recovery of Band-Edge Emission in InAs Nanowires through Surface Passivation, Nano Lett., *12* (7), pp 3378–3384 (2012)
14. T. Takahashi, P. Nichols, K. Takei, A. C. Ford, A. Jamshidi, M. C. Wu, C.Z. Ning, A. Javey, Contact Printing of Compositionally Graded CdSxSe1-x Nanowire Parallel Arrays for Tunable Photodetectors, Nanotechnology, 23，045201（2012）
15. X. Zhuang, C.Z. Ning, A. L. Pan, Composition and Bandgap-Graded Semiconductor Alloy Nanowires (Invited Review), Adv. Mater., 24, 13(2012)
16. Z. C. Liu, L. J. Yin, H. Ning, Z. Y. Yang, L. M. Tong, and C. Z. Ning, Dynamical Color-Controllable Lasing with Extremely Wide Tuning Range from Red to Green in a Single Alloy Nanowire, *Nano Lett.*, 13 (10) (2013), pp 4945–4950
17. F. Fan, Z. Liu, L. Yin, P. L. Nichols, H. Ning, S. Turkdogan and C. Z. Ning, Simultaneous two-color lasing in a single CdSSe heterostructure nanosheet, Semicond. Sci. Technol. 28 (2013) 065005

Invited Presentations

1. C.Z. Ning, Nanophotonics with Nanowires and Plasmonics, Keynote talk, at The Second International Conference on Manipulation, Manufacturing and Measurement on the Nanoscale, 29 August –1 September2012, Xi'an, China
2. C.Z. Ning, Nanophotonics with Nanowires and Plasmonic Shells, Hong Kang Polytech University, May 22, 2012
3. C.Z. Ning, Semiconductor Alloy Nanowires for Optoelectronic Applications from UV to IR, Seminar at School of Nanoscience and Technology, Suzhou University, Suzhou, China, June 4, 2012
4. C.Z. Ning, Semiconductor Alloy Nanowires and Plasmonic Nanostructures for Nanophotonics, Colloquium of Department of Optoelectronics, Zhejiang University, Hangzhou, China, June 7, 2012
5. C.Z.Ning, Composition Graded II-VI and IV-VI Nanowires for Full-Spectrum Optoelectronic Applications from UV to Mid-IR， InternationalWorshop on 6.1A II-VI and III-V Materials and Their Integration, Tempe, AZ, Nov 2011
6. C.Z. Ning, Semiconductor Alloy Nanowires for Optoelectronics Applications from UV to Midinfrared, Material Science Seminar, University of Wisconsin Madison, Sept 29, 2011
7. Cun-Zheng Ning, Derek Caselli, Ding Kang, Debin Li, Zhicheng Liu, Patricia L. Nichols, Minghua Sun, Leijun Yin, Nanophotonics with Plasmonics and Nanowires: Applications

to Subwavelength Lasers and Novel Solar Cells, Villa Conference on Interactions Among Nanostructures, April 21-25, 2011 Las Vegas, Nevada

8. C.Z. Ning, Alloy semiconductor nanowires for optoelectronic applications from UV to IR, March 16, 2011, Lecture, EECS Department, UC Berkeley
9. C.Z. Ning, Semiconductor alloy nanowires and applications to high efficiency solar cells, AZ Nanotech Council, Feb 24, 2011
10. C.Z. Ning, Nanophotonics with Plasmonics and Nanowires: Applications to Subwavelength Lasers and Novel Solar Cells, Symposium on Nanophotonics and Renewable Energy, Chinese Acandemy of Science, Institute of Physics, Jan 17-18, 2011
11. C.Z. Ning, Quaternary semiconductor alloy nanowires for full-spectrum optoelectronics, invited lecture at iNOW 2010, Beijing/Changchun, Aug. 1-13, 2010
12. C.Z. Ning, Semiconductor Nanolasers with Nanowires and Plasmonic Shells, Institute of Physics, Chinese Academy of Sciences, May 20, 2010
13. C.Z. Ning, II-VI Semiconductor Alloy Nanowires for Full-Color Light Emitting and Lasing, Invited talk at ISSLED 2010 Beijing, May 21, 2010
14. C.Z. Ning, Semiconductor Alloy Nanowires and Their Applications in Full-Color Optoelectronics, College of Materials Sciences, Beijing Institute of Technology, May 20, 2010
15. C.Z. Ning, Progress in Nanophotoncis, Physics Department, Northwestern Polytechnique University, Xian, China, May 14, 2010
16. C.Z. Ning, Recent Progress in Nanophotonics Materials and Nanophotonics, Xian Jiaotong University, Xian, China, May 13, 2010
17. C.Z. Ning, Semiconductor alloy nanowires and their application in photovoltaics, Physics Colloquium, Arizona State University, March 25, 2010
18. C.Z. Ning, Nanolasers with Wires and Plasmonic Shells: How Small Can They Be?, Seminar at IEEE Photonics Society CREOL Chapter, University of Central Florida, March 17, 2010
19. C.Z. Ning, CVD Grown Composition-Graded Ternary and Quaternary Allow Nanowires, University of Florida Chemical Engineering Department Seminar, March 15, 2010
20. C.Z. Ning, Erbium Silicate Single-Crystal Nanowires for Silicon-based Light Emission, Seminar at Intel Corporation, Santa Clara, CA, Feb 5, 2010

Paper submitted:

1. P. L. Nichols, Z. Liu, L. Yin, and C. Z. Ning, $Cd_xPb_{1-x}S$ Alloy Nanowires and Heterostructures with Simultaneous Emission in Mid-Infrared and Visible Wavelengths, submitted

Abstract

Extensive research has been conducted in growing and characterizing semiconductor nanowires, especially in demonstrating unique lasing capabilities of our nanowire materials and structures. The key results achieved include a novel growth method strategy that is termed “dual-gradient method”, which combines the temperature gradient with source (precursor) material composition gradient to optimize the growth condition for semiconductor alloy nanowires. This dual gradient method has been utilized to grow a wide range of novel alloy semiconductor nanowires and led to a wide array of new nanomaterials such as first quaternary semiconductor alloy nanowires, spatial-composition graded alloy nanowires with emission covering the complete visible spectrum emission from a single substrate, and widely tunable lasing on a single substrate from 500 to 700 nm. The possibility of such novel materials to be used for novel solar cells was also explored, with some basic design, simulation demonstrated, and preliminary fabrication undergoing. More recently the further exploration of such growth has led to the first dual-color (red and green) lasing from a single nanosheet and dynamically tunable color lasing between green and red from a single nanowire. Such unique functionalities were all enabled because of the novel method being developed and the novel materials grown as a result. Many of the demonstrated lasing capabilities are novel and impossible with the traditional planar epitaxy technologies. We believe that such novel functionalities demonstrated provide basis for more applied research projects in the future to further develop them into more practical devices and real world solutions for the DOD and for the commercial world.

The second part of the work for the extension period involved investigation of electrical injection single nanowire laser work. Extensive design and fabrication study has been conducted. While our designs have shown great promise and various fabrication steps have been verified, a working electrical injection laser has not been achieved. Apparently the time and efforts needed are beyond what was possible under the present support. This subject remains a challenge for the entire community, since no other group has been able to demonstrate a single nanowire lasing under electrical injection 10 years after the first experimental work was published. We believe that we have gained a lot of understanding of the issues involved. Our design and fabrication process have potential advantages over many other approaches available in the literature. The related research is still on going with a reduced level of efforts without external funding, in informal collaboration with a few international groups.

Summary Description of Major Research Results

1. Lasing demonstration using individual PbS nanowires: In the proposed efforts, we have

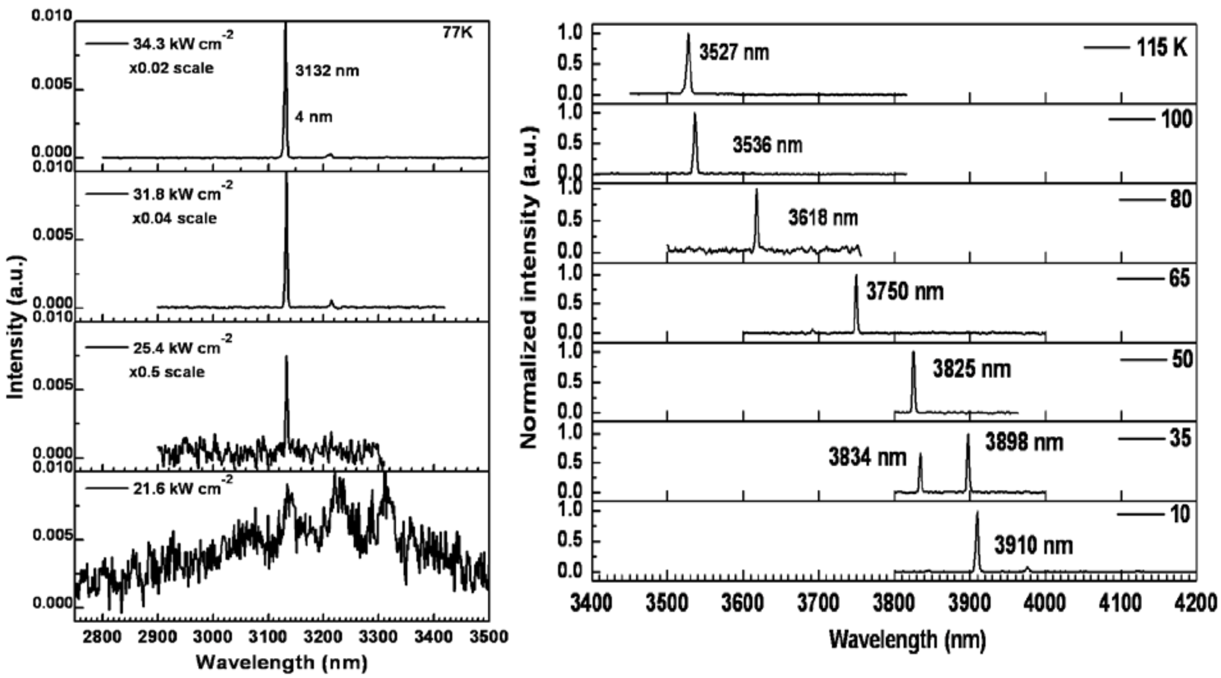

Figure 1 PL spectra of as-grown PbS wires on Si substrate with increasing pump power at 77K (left), showing transitions from spontaneous emission to lasing, and for several temperatures from 10K to 115K (right)

mostly concentrated on visible and short wavelengths and have successfully achieved alloys of ZnCdSSe to have the light emission or lasing covering the entire visible spectrum, as reported elsewhere in this proposal. To expand the wavelength to longer wavelength, we started to alloy CdS with PbS, since PbS has a bandgap in the midinfrared (4 microns), this alloy would allow us to eventually cover wavelength range between 500 nm and 4 microns. Such material would have a lot of applications in mid-infrared lasing, solar cells and multi-wavelength detectors (visible and MIR). As a first step, we were able to grow high quality PbS microwires of several tens of microns in length. Such wires have one of the best light emission properties compared to other materials of this wavelength range. As a result, we were able to demonstrate lasing of a single such wire up to 115K. As shown in Fig. 1, a single-mode lasing peak around 3.1 microns with peak width of 4 nm was observed from as-grown PbS wires on Si substrate at 77K. The lasing threshold has a value around 3.3 $kWcm^{-2}$, which is also among the lowest threshold compared to other wires. This work on PbS wires represents the longest wavelength lasing from nanowires ever demonstrated.

2. Systematic understanding of PbS growth mechanism

Understanding the growth mechanisms of semiconductor nanowires is important for the long term goal of developing devices based on such nanomaterials. To this end, growth modes of PbS wires were systematically investigated under different growth conditions. Three distinct growth modes were indentified, including vapor-liquid-solid (VLS) growth of wires directly from the substrate, VS deposition of bulk crystallites, and subsequent VLS wire growth on top of the bulk crystallites, as shown in Fig. 2. The dominant growth modes were related to source vapor supersaturation levels, which is important information for the design of experiments to create wires of desired morphologies.

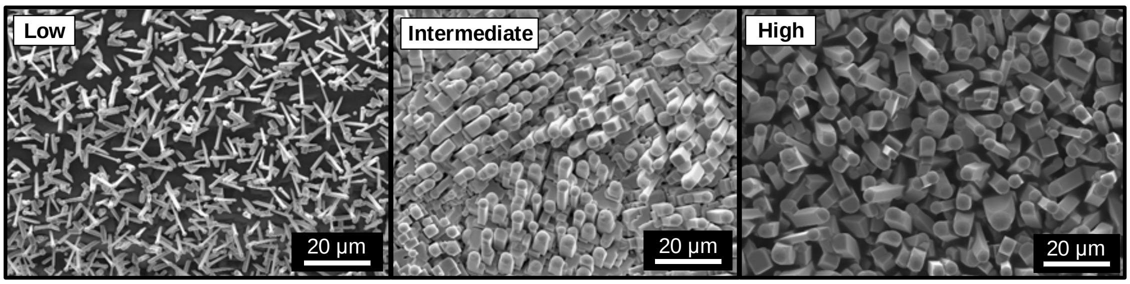

Figure 2: PbS wires with various supersaturation levels and corresponding morphologies: low supersaturation with VLS growth of wires from substrate, intermediate supersaturation with oriented VLS wires grown on top of large bulk crystallites, and high supersaturation with randomly oriented VLS wires on top of bulk crystallites.

3. CdS-PbS and CdS-CdSe Alloying and Spatial Orientation by Contact Printing (Collaboration with Javey's group at Berkeley)

a. CdS-CdSe Alloy Growth for Contact Printing

CdS-CdSe alloy growth by the dual gradient method was optimized to maximize the growth of nanowires instead of nanobelts in the Se-rich regime. The alloy gradient wires were contact printed onto a receiver substrate to align the wires for potential device applications.

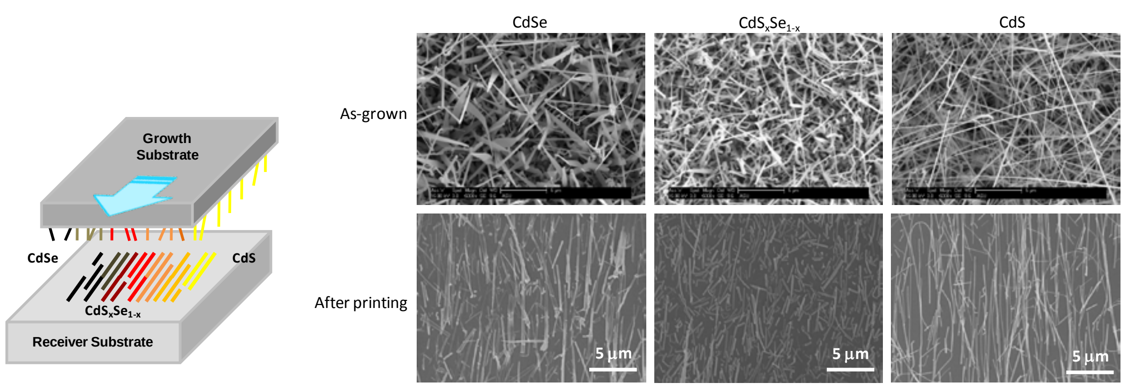

Figure 3: Schematic diagram of contact printing process (left) and SEM images (right) before (top) and after (bottom) contact printing.

b. PbS-CdS Alloy and Heteostructure Nanobelts

PbS-CdS alloying experiments resulted in nanobelts which appear to have an interface or heterostructure-type morphology between Pb-rich and Cd-rich regions. PL characterization in the visible spectrum indicated a CdS-rich alloy with a 544 nm bandedge emission peak, shifted from pure CdS bandedge emission at 512 nm, and very strong surface states around 690 nm which is shifted from PbS bandedge.

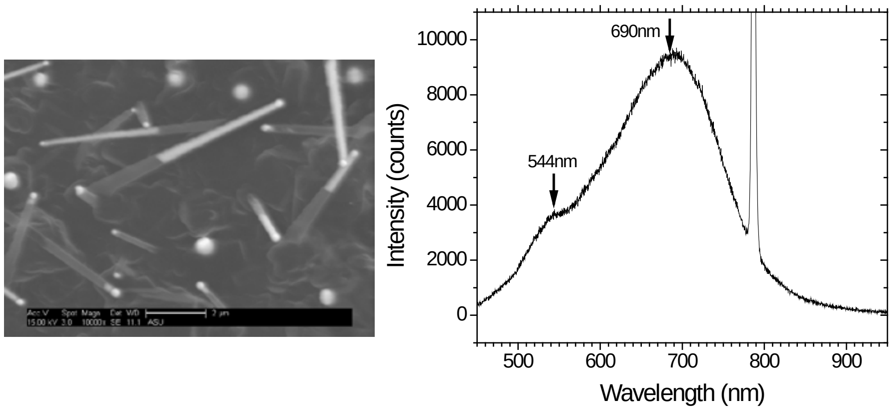

Figure 4: SEM (left) and PL (right) of PbS-CdS alloy nanobelts. The contrast change in the SEM indicates the heterostructures formed with alloys of two different compositions.

A pressure shutter method was implemented to increase interaction between source vapors during growth. XRD of the nanobelts on textured film showed both cubic and hexagonal phases of CdS, in addition to peaks located between the reference pattern peaks for PbS and CdS, indicating a solid-solution alloy phase. The solid-solution alloy phase is an important demonstration of alloying efforts towards an alloy gradient between PbS and CdS.

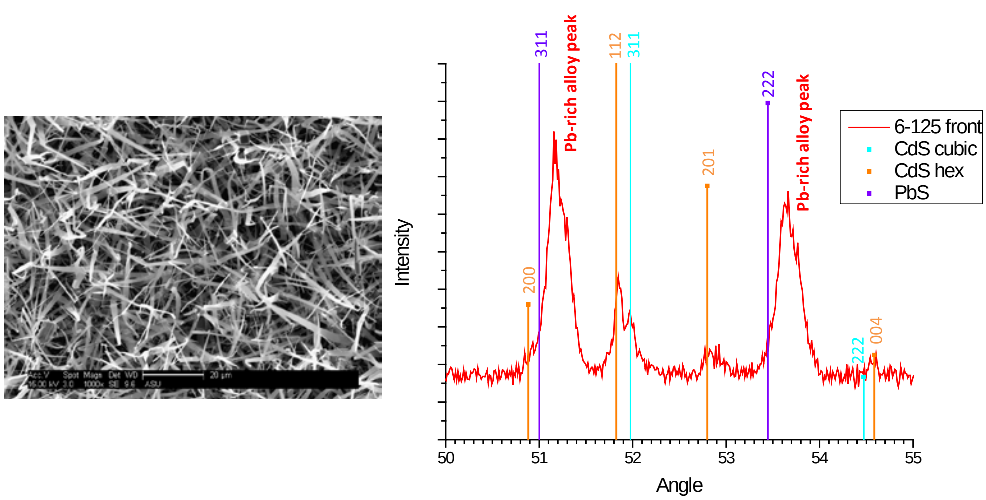

Figure 6: SEM (left) and XRD (right) of PbS-CdS alloy nanobelts and textured film.

Alloying of CdS and PbS could potentially provide an important semiconductor with a wide range of bandgaps, with bandedge emission from mid-infrared to visible green, for various optoelectronic applications. We have investigated the possibility of PbCdS alloy formation in nanowire and nanobelt forms, especially the dependence of alloy composition on two different cooling routes. Our results show that rapid cooling immediately after the growth phase can lead to a high-quality uniform alloy with Cd composition larger than possible at thermal equilibrium and by natural cooling. On the contrary, unassisted natural cooling leads to the formation of axial or core-shell heterostructures, containing segments with pure CdS and PbCdS alloys with lower Cd content than through rapid cooling. Such heterostructures with green and mid-infrared emission provide simultaneous access to two widely separated wavelengths from a single monolithic structure and can be important for many applications. Our results can help identify strategies for growing nanostructures with uniform alloy of high Cd incorporation, core-shell structures with shell serving as a passivating or protecting layer, or interesting longitudinal heterostructures. Both various heterostructures and uniform alloys of these materials could be important for high-efficiency solar cells, novel detectors, and nanolasing in wide spectral ranges.

c. Multi-Colored Nanostructures from PbS-CdS Growth

Initial efforts of using the dual gradient method to create PbS-CdS alloy gradient samples resulted in substrates with multi-colored areas, including an orange region with long, textured wires with significant EDS Pb signal. The orange region does not have PL signal in the visible range. Peaks around 2350 nm and 2100 nm were observed, which are significantly blue-shifted from the pure PbS peak. The visible orange color is not due to the change in band gap due to alloying, instead possibly due to a light scattering effect.

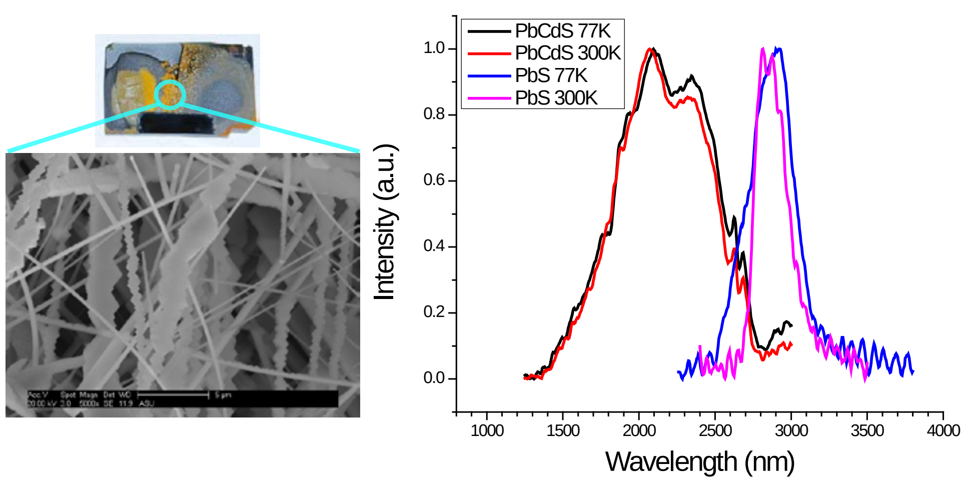

Figure 7: Color photograph (top left), SEM (bottom left), and PL spectrum (right) of PbS-CdS alloy wires with comparison to pure PbS signal.

4. Templated Growth (in collaboration with Javey of Berkeley and Xiuling Li of UIUC)

a. Au-Assisted Etched Si Template

Template arrays were created by Au-assisted etching. SEM imaging after CdS growth shows many nucleated CdS wires with some wires extending out of the pores. Work is ongoing to optimize the etching process for repeatable arrays and to optimize the CdS growth parameters for large diameter wires and high-yield growth with one wire per pore.

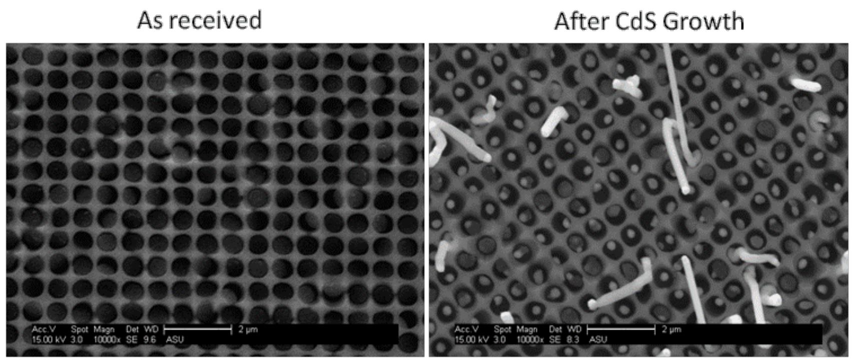

Figure 8: SEM images of Si template before (left) and after nanowire growth (right). Some nanowire overgrowth is visible which can be removed by cleaning with ion beam.

b) Arrayed Nanowire Growth Based on Anodic Aluminum Oxides

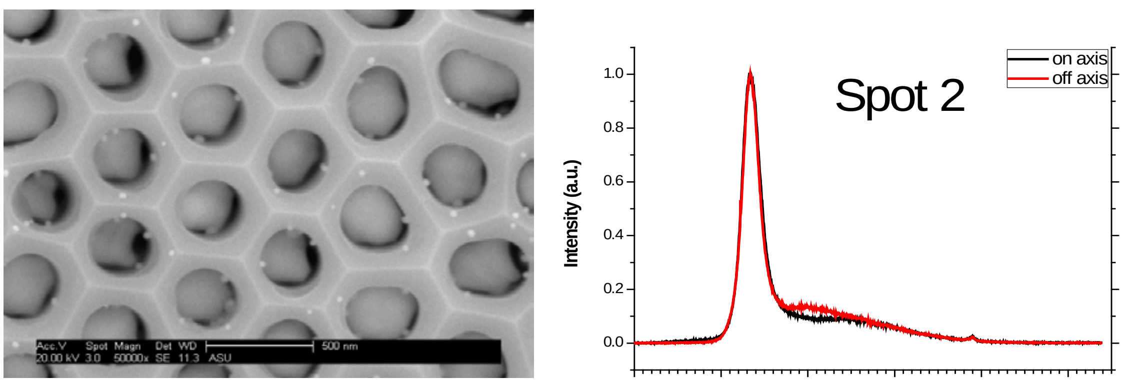

Figure 9 (left) Templated growth of CdS nanowire arrays from the AAO pores. (right) PL spectra measured with different excitation angles, the narrow linewidth showing good quality of wires.

To make our unique nanowires compatible the standard fabrication technique of optoelectronic devices, vertical array of nanowires will be preferred. With the AAO template provided by Javey's group at Berkeley, we have successfully grown array of CdS nanowires from the AAO pores, as shown in Fig.3. PL measurement showed that the wires are of high crystal quality, showing PL spectrum near the bandgap with width as narrow as the PL grown without AAO. The purpose is to be able to control the orientation of nanowires and achieve regular arrays for many applications. Currently we are working to improve the growth and increase the wire height.

5) Super Broadly Continuously Tunable Lasing between 500-700 nm on a Single Chip

By taking advantage of the temperature dependence of the alloy composition as a function of local growth temperature on a substrate in a CVD growth, we engineered a temperature gradient along the axial direction of a CVD reactor where we positioned a 1.2cm long substrate. In a CVD growth, we placed CdS and CdSe powders near the center of a CVD reactor where the temperature is around 1000 degree Celsius. The chemical valor containing Cd, S, and Se was then transferred using the carrier gas to the downstream of the reactor and then deposited onto the substrate. Due to the temperature dependence of the incorporation rates of different elements into the ternary alloy CdSSe, a spatially varying ratio of S/Se is achieved, resulting a complete composition range from pure CdS to pure CdSe via CdSSe along the length of the substrate. The corresponding bandgap change is reflected on the color change in the substrate as shown in Fig.1.

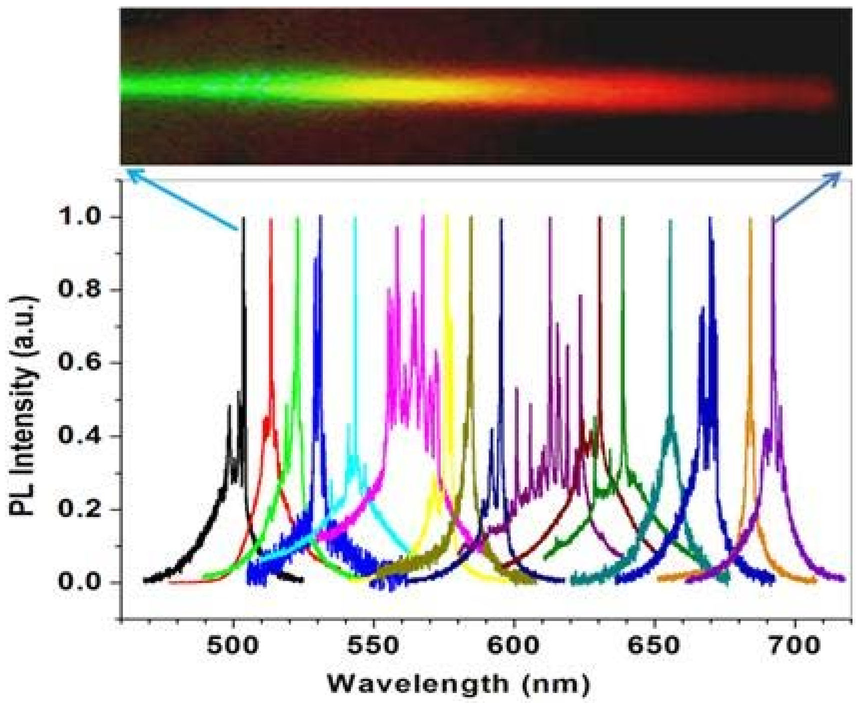

Figure 10 Real color image of nanowire sample of 1.2 cm long (top). The color change is a result of bandgap changing from left to right. This was made possible through a composition grading of alloy composition. Spatial-resolved microscope photoluminescence collected at 16 points along the length of the substrates (bottom). The sharp spectral lines indicate lasing action already happened at high optical pumping.

The single crystal ternary alloy deposited has a high quality, as evidenced by the PL measurement which showed strong bandgap emission. The interesting result of this work was the demonstration of lasing with a tunable wavelength between 500 nm and 700 nm, corresponding bandgap lasing of CdS and CdSe respectively. This is by far the widest wavelength tuning on a single substrate in any semiconductor lasers and the results were published in Nano Letters (paper 2 of the Papers Published). The results were widely reported in technology Magazines (such as R & D Magazine, Laser Focus etc) and Websites (optics.org etc).

6). First demonstration of quaternary alloy nanowires and nanobelts.

Since our ultimate goal of this project is to realize tunable lasers with wavelength from red to blue and UV. It was necessary to incorporate widegap compound such as ZnS into our spatially graded alloy study. We used an improved co-thermal evaporation route to achieve for the first time quaternary alloy semiconductor nanostructures, using $Zn_xCd_{1-x}S_ySe_{1-y}$ nanobelts as an example. The composition of the achieved alloys can be tuned by controlling the molar ratio of the source materials, resulting in their bandedge light emission to be continuously tunable across the entire visible spectrum. This material system in its complete bandgap range has never been

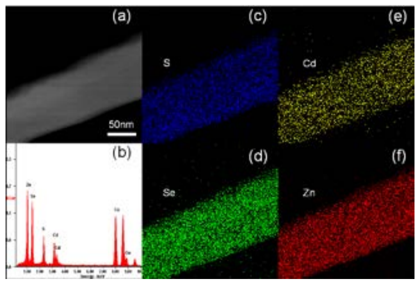

Figure 11 (a)TEM image of an examined quaternary belt and its corresponding energy dispersive x-ray diffraction elemental profile measured from a point in the belt; (c)-(f) The 2D element mapping for the detected four elements, Zn, Cd, S and Se, respectively.

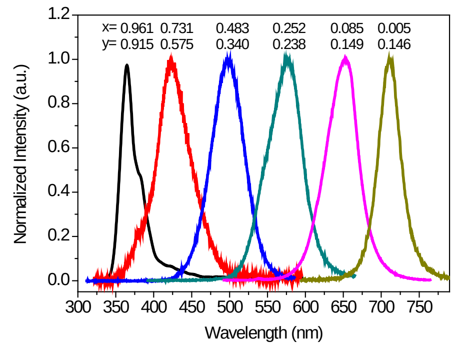

Figure 11 (b) The normalized PL spectra of the achieved quaternary ZnxCd1-xSySe1-y nanobelts excited with a pulsed frequency-quadrupled Nd:YAG laser (266 nm). The data above the spectra show the relative composition x and y values.

achieved in any form of single crystals, bulk or nanomaterials. Such composition widely controlled alloy nanostructures provide a new material platform for a wide range of applications from wavelength-tunable lasers, multicolor detectors, full-spectrum solar cells, LEDs to color displays, many of which are under active pursuit currently.

7.) Spatial alloy composition grading over the entire visible spectrum

In section 1), we reported the composition grading to produce bandgap change corresponding to the wavelength range from 500nm to 700 nm. In section 2), we reported the first quaternary alloy nanowires with bandgap emission from UV to red over the entire visible spectrum where each individual composition (bandgap) is produced by a separate growth. It is

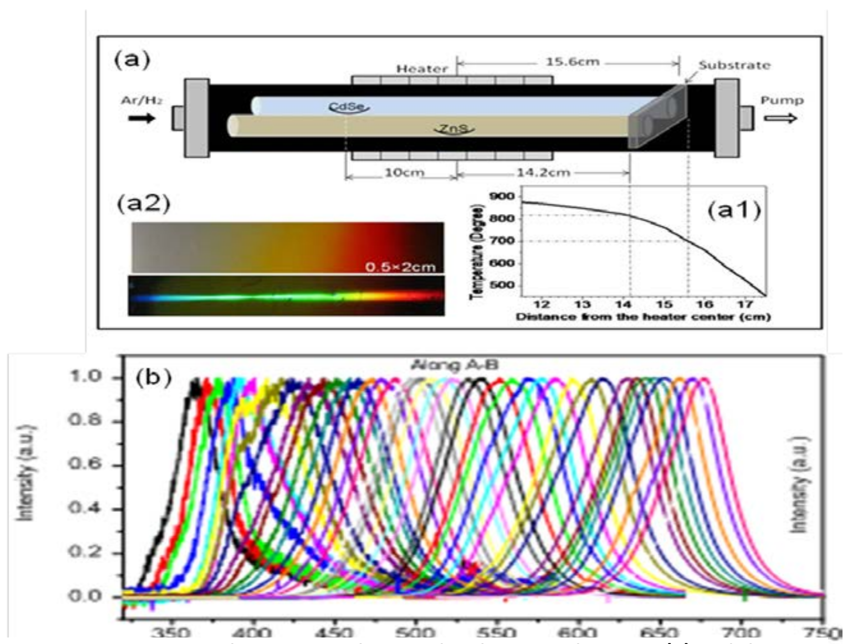

Figure 12 CVD setup with two minitubes inside a horizontal reactor (a) and the micro-PL measurements at 40 locations along the length of the nanowire wafer substrate (b), showing the bandedge emission changing from UV to red as a result of bandgap grading. Inset (a1) shows the temperature profile and inset (a2) shows the real color pictures of as grown sample under room lighting (top) and under a UV illumination.

natural to ask if the entire visible spectrum range could be produced by *a single growth* using spatial composition grading as in Section 1). While such composition grading was done in the case of section 1) using temperature grading (TG), it turned out very difficult to achieve this over the entire visible spectrum by using TG alone. A method used recently by a group at Berkeley was to use three mini-tubes inside a big horizontal reactor (see Fig,3), where different source materials were placed inside different mini-tubes. The spatial configuration of mini-tubes determines the spatial profile of the deposited materials on a substrate. We call this method source material profiling (SMP). In the Berkeley experiment, the temperature gradient was not exploited. Our experiment showed that the pure SMP alone was not enough to grow high quality crystal either. After repeated experiments, it turned out that a combination of the Berkeley SMP and our TG is a perfect method to achieve the alloy composition grading over the entire visible spectrum. The setup and the PL spectrum are shown in Fig. 3. Furthermore, we believe that this approach is a more general approach that can be used for other materials systems to achieve spatial alloy composition grading. This material has some potential unique applications in solar cells and in multi-spectrum detectors. These applications will be also explored in the future.

8.) Simultaneous Green and Red Lasing from a Single Hetero-structure Nanosheet

While we have previously demonstrated multi-color lasing on a single substrate in a single CVD growth, but the multicolor lasing were from many nanowires. For many applications, it is more important to be able to achieve lasing from a single nanostructure. Using a novel growth technique, we were able to grow CdS and CdSe into a single hetero-structure.

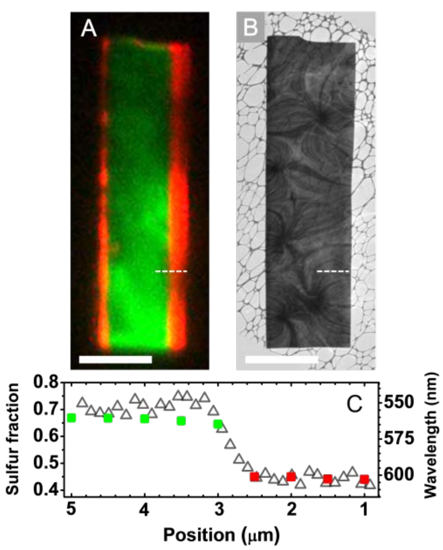

Figure 13 (A) Real-color PL image of a CdSSe lateral heterostructure nanosheet excited by 405 continuous-wave laser. (B) TEM image of the same nanosheet. The scale bars in (A) and (B) are 10 μm. (C) Comparison of sulfur molar fraction between EDS scan (hallow triangles) and micro-PL scan (solid squares) along the white dashed line in (A) and (B).

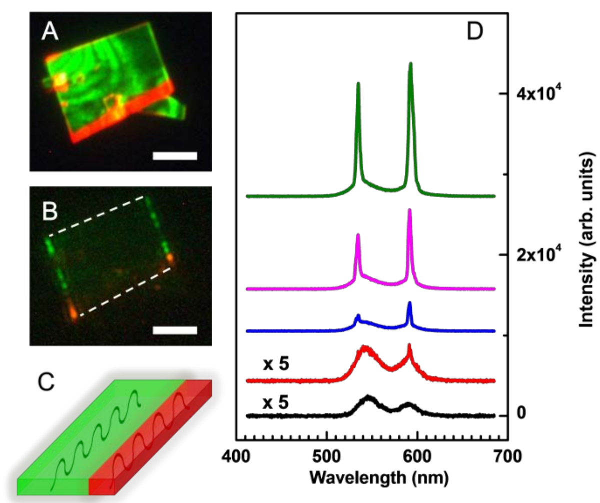

Figure 14 Real-color PL image of the nanosheet under low pumping power density at room temperature (A) and under 409 kW/cm^2 at 77K (B). The dashed lines in (B) denote the side edges of the nanosheet. The scale bars in (A) and (B) are 10 μm. (C) Schematic diagram of the nanosheet waveguide structures. (D) PL spectra at 77K under increasing levels of pumping power density of 77, 173, 241, 338 and 668 kW/cm^2 from bottom to top.

9.) Multi-Color Lasing and Dynamical Color Control in a Single Nanowire

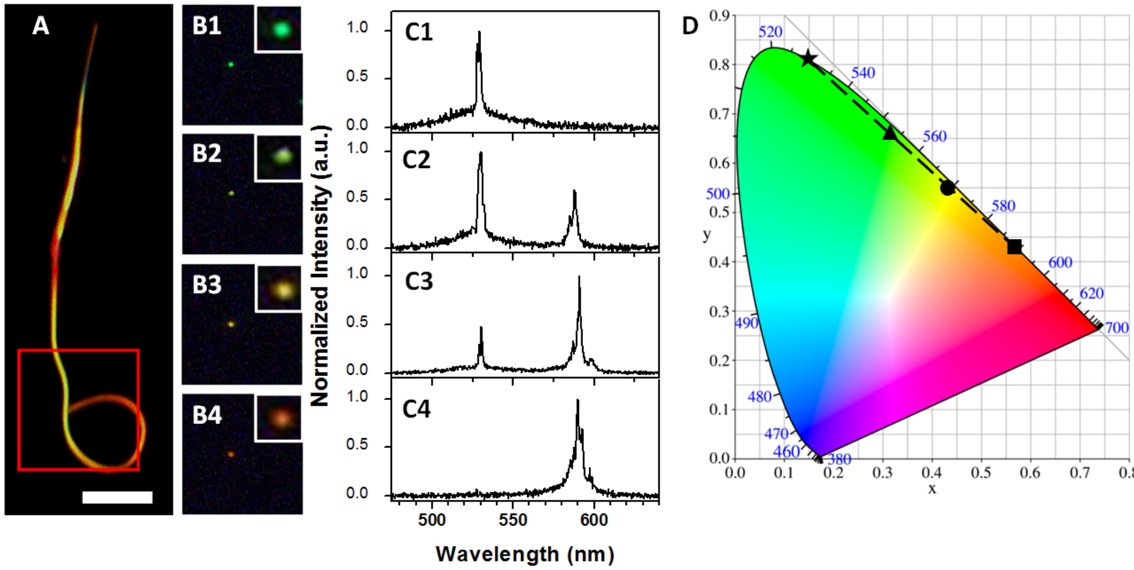

Figure 15. Color control of a looped wire dual color laser. **(A)** Dark field image of the looped nanowire, where the scale bar is 10 µm. Two excitation beams are focused to less than 40 µm spot size to the looped and straight sections respectively. **(B1-B4)** Real color images of the lasing under different pumping for the two cavities. The images are taken from the red box in A. The bright spots correspond to the junction of the loop. The insets show the zoom-in images of the junction lasing spots. **(C1-C4)** Normalized lasing spectra under different controlled pumping intensities, collected simultaneously with the images of C1-C4. The intensity ratios of the green and red modes in C1-C4 are 10:0, 6:4, 3:7 and 0:10, respectively. **(D)** The calculated colors from the spectra in C1-C4 plotted on CIE1931 color space. Star (★), triangular (▲), circle (●) and square (■) labels correspond to C1-C4, respectively.

Alloy nanowires with composition graded or controlled along the wire axis have been demonstrated. But multi-color lasing from such wires has been difficult due to the absorption of short wavelength emission by narrow gap segments on the same wire. However, by looping the widegap end of the wire into a closed circle (see Fig.15 A)), a separate cavity can be formed that will confine the short-wavelength emission without being strongly absorbed by the narrow gap section. In such a partly looped structure consisting of a straight section and a looped section, the entire wire still forms a cavity for the long wavelength, but the looped cavity will mainly form a cavity for the short wavelength. In this way, both long and short wavelengths can achieve lasing. Thus from the straight end, only long-wavelength (red) can be measured. But from the short-wavelength end, both colors can be measured. Thus the light emission from the short-wavelength end is a mixture of both colors. Furthermore, when the two cavities are pumped separately with varying intensities, the resulting colors from the short-wavelength ends can be varied over in a wide range between the short-wavelength and long-wavelength. As we can see from the figure, the color of our laser can be controlled from red to green. Such dynamical color control could be eventually used for display and other applications including multi-color fluorescence imaging.

10). Design and Fabrication Study of Electrical Injection Nanowire Lasers

Extensive design, simulation, and fabrication study have been carried out to identify a complete process that would lead to an electrical injection single nanowire lasers. A simplified version of

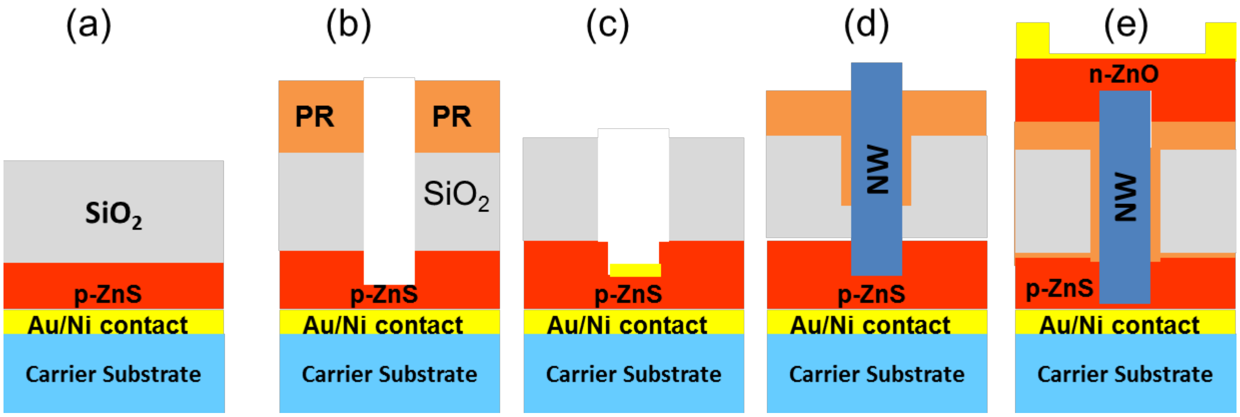

Figure 16: Fabrication process identified a). Deposit Au/Ni contact metal on substrate, Evaporate p-ZnS:Cu; Grow 3-5 μm thick SiO_2 by plasma enhanced chemical vapor deposition. b) Spin coat photoresist (PR) and photolithography to define template pattern; RIE SiO_2 using PR as mask.; further continue to dry etch ZnS (2-300 nm); c) Dip sample in HF to enlarge the hole ; deposit gold catalyst; remove PR top; d) CVD growth of nanowires; Spin SU8 resist the fill the voids around nanowires; planarize sample, leaving 200 -300 nm of nanowire outside SU8; e) Sputter n-ZnO; deposit a thin Ti/Au on top and then deposit thicker Au ring contact elsewhere of the sample to make thick enough electrode.

this process is shown in Fig. 16. The final electrical injection laser is shown in Fig.16 (e). The essence of the final device is explained in the following: The intrinsic nanowires can be CdS, CdSe or their alloys that constitute the gain materials. The p- and n-contact materials are fabricated using standard thin-film technology and are outside of nanowires, avoiding the complication of nanowire doping, which is still difficult to control. Also such design allows the utilization of other doped materials that are available, giving more flexibility in the choice of doped contact materials. The waveguides are mainly the high index nanowires that are surrounded by lower index oxide. The metal on both ends of nanowires will serve as high reflective mirrors forming both ends of the nanowire-laser cavity. Detailed numerical simulation verifies the design, as shown in Fig.17, where modal Q values and wavelengths are shown for CdS and CdSe nanowires. The threshold gain and voltages are shown in Fig. 18 for both nanowires as function of nanowire length.

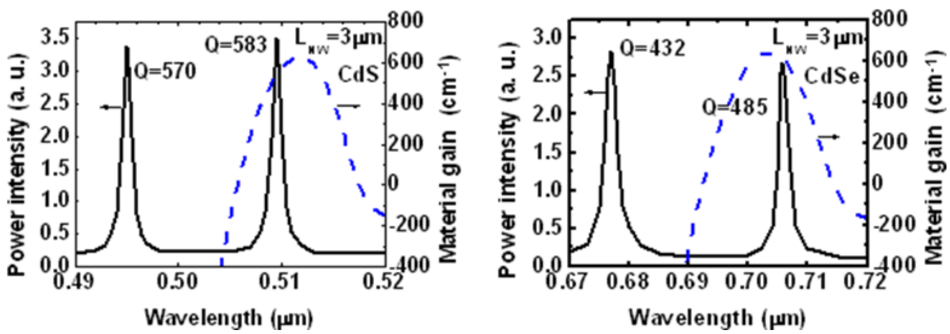

Figure 17 Simulation of modes and their Q-values for CdS (left) and CdSe (right) nanowires, where the length of nanowires is 3 microns. The material gain spectrum is also shown in each case with blue dashed line, indicating the spectral overlap with one of the modes.

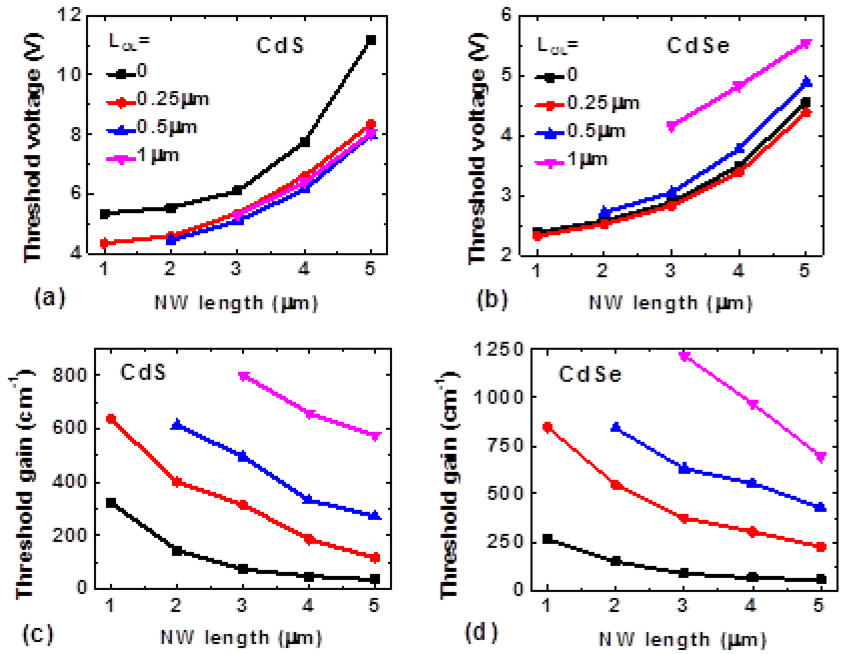

Figure 18 Threshold voltage (a and b) and gain (c and d) are shown from simulation as function of nanowir length, showing that reasonable levels of the threshold gain can be achieved with our design.

Various fabrication experiments have been conducted to test the feasibility of the proposed approach. But the fabricated devices have not been able to show expected behavior, or produce a lasing device, due to the limited time and resources. Experiments are still on going on a reduced scale.